

# Linearity test

in compliance with the norm NF\_EN\_14662-3 2015

Chromatotec®

# Test description

- Description of the test in the chapter 9.6.2.

*“The linearity deviation of the analyzer shall be investigated using at least the following concentrations: 0%, 10%, 50% and 90% of the maximum value of the certified measuring range of benzene or the range defined by the user (see 9.5.1). For each concentration (including zero), at least 3 measurements must be made, the first result must be eliminated.”*

<b>Linearity (on site test)</b>	<b>C(<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>C(ppb) (at 20°C)</b>
0%	0	0.00
10%	5	1.54
50%	25	7.69
90%	45	13.85

# Test description

- Description of the test in the chapter 9.6.2.

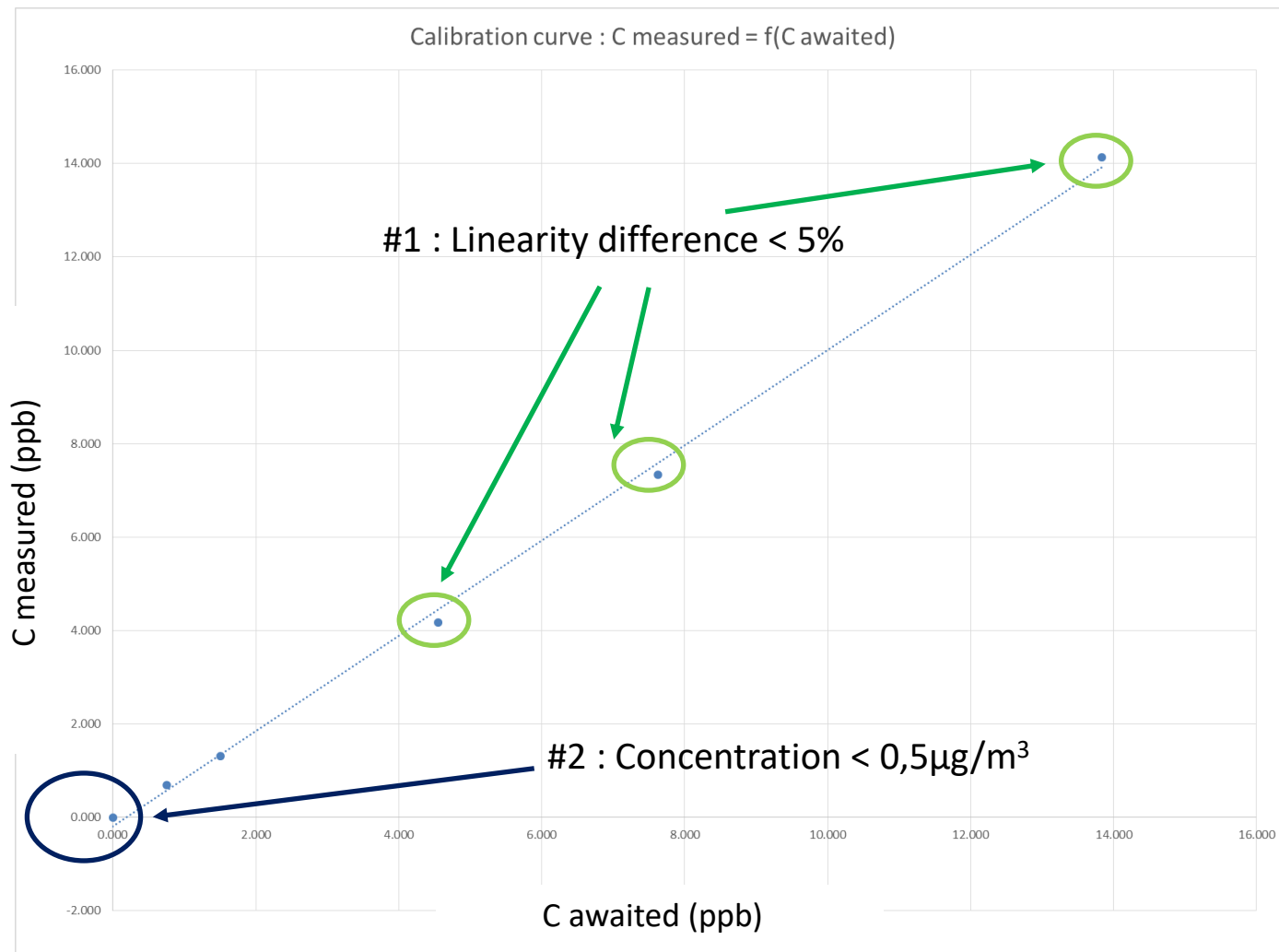
After drawing the calibration curve :  $C \text{ (measured)} = f(C \text{ awaited})$

Two criterions to check to pass the test:

- ✓ #1 : For each concentration :
  - Linearity difference  $< 5\%$
- ✓ #2 : Intercept of the calibration regression line :
  - Concentration  $< 0,5\mu\text{g}/\text{m}^3$

# Test description

- Description of the test in the chapter 9.6.2.



## Diluting system to be used for this test

- Description of the diluted system required to start the linearity test (cf norm):

*“For applied concentrations, the relative uncertainty from a dilution ratio to another must be less than 1.5%.”*

Important remarks:

It is very difficult to be sure the dilutor used fulfills this requirement :

- How to verify the uncertainty is less than 1,5%?
- What kind of tests allows us to quantify this uncertainty?
- What kind of instrument using to quantify this uncertainty?
- Do not confuse the uncertainty of the flow fixed by one MFC and the uncertainty of the whole dilution system (2 MFCs, homogeneous mixture, adsorption of the compounds on the tubes...)

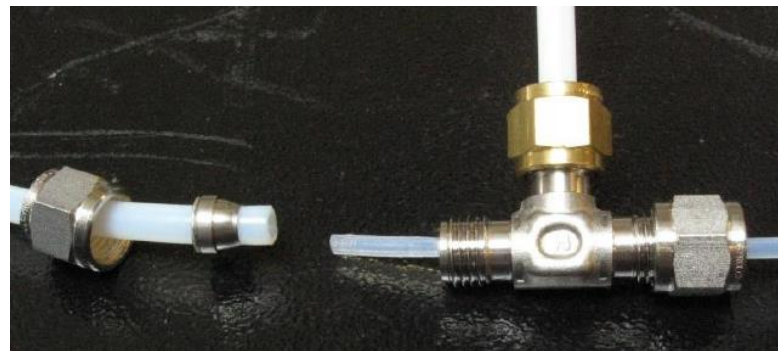
# Tools used by Chromatotec for the test

- Dilution system with:

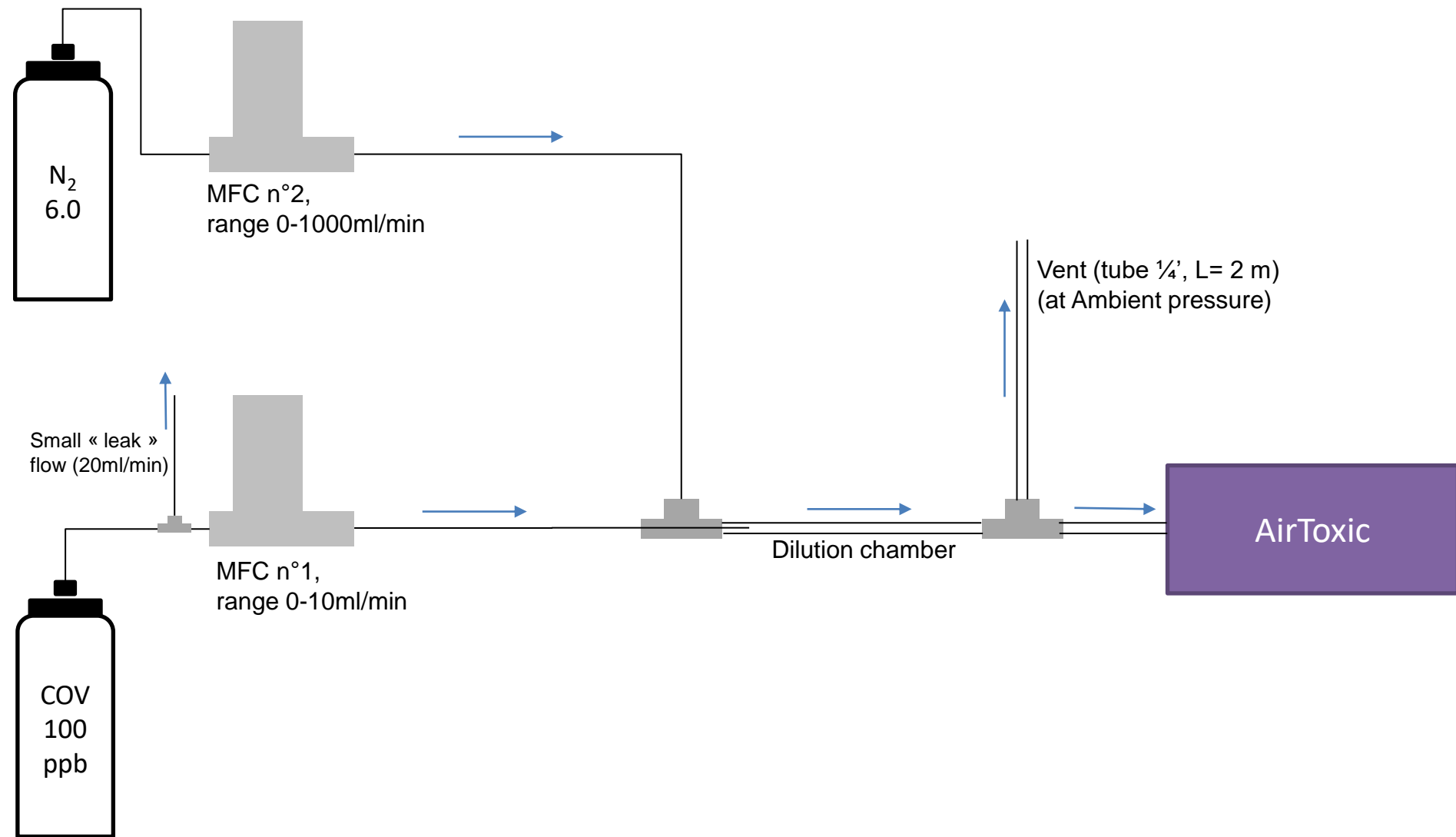
- ✓ Cylinder containing BTEX (100ppb),  $N_2$  matrix
- ✓ Two Mass Flow Controllers
- ✓ MFC n°1 : Bronkhorst range 0-10mL/min
- ✓ MFC n°2 : Bronkhorst range 0-1000mL/min
- ✓ Carrier gas of GC :  $N_2$  6.0
- ✓ Gas used for the dilution :  $N_2$  6.0
- ✓ All the flows are verified using BIOS flowmeters (precision : 1% read value): two flowmeters are used : range 5-500mL/min and 50-5000mL/min.
- ✓ The vent tube is always at ambient pressure

- Dilution chamber:

- ✓ PTFE Tube ¼"
- ✓ Stainless steel fittings
- ✓ Length = 20cm
- ✓ "special mixing "Te" connector:



# Tools used by Chromatotec for the test



# Precautions to take before starting the test

- Concerning the dilution system:
  1. Flows have to be in the range of each MFC :  $10\% < \text{flow} < 90\%$  to have a good regulation.
  2. The gas pressure feeding each MFC has to be perfectly stable, to have a stable flow at the MFC outlet.
  3. Purge the VOC cylinder 3 times before connecting it to the MFC
  4. If you use gas generator for the dilution, add a pressure regulator before the MFC to optimize the flow stability on the MFC
  5. Use a "leak" flow of pure VOC gas (around 20mL/min), just before the MFC n°1 to reach a stable mixture quickly
  6. Do not use flows bigger than 1.5L/min at the dilutor outlet to ensure a perfect mixture
  7. Check carefully the pressure at the sampling point is always at ambient pressure (check Ambient pressure displayed on Vistachrom), even for the strongest dilutions applied (with the highest flows).
  8. During this test, be aware of the unit used :

Flows always displayed in the same unit on your flowmeter (mL/min standard conditions,...)

Conversion mg/m<sup>3</sup> into ppb(v) always done with the same molar volume (at 20°C, 1013hPa)
  9. During your dilution, check that for one dilution point, the concentrations used are stable (more explanations on the next slide)



# Precautions to take before starting the test

- Number of repetitions for each dilution point:

All the diluting system needs time to reach a stable state : homogeneous mixture, passivation of the tubes... This time (only caused by the diluting system) must not impact negatively the tests relative to the GC linearity.

- A classic result often obtained:

⇒ Phenomenon mainly created by the dilutor, not the GC!



# Precautions to take before starting the test

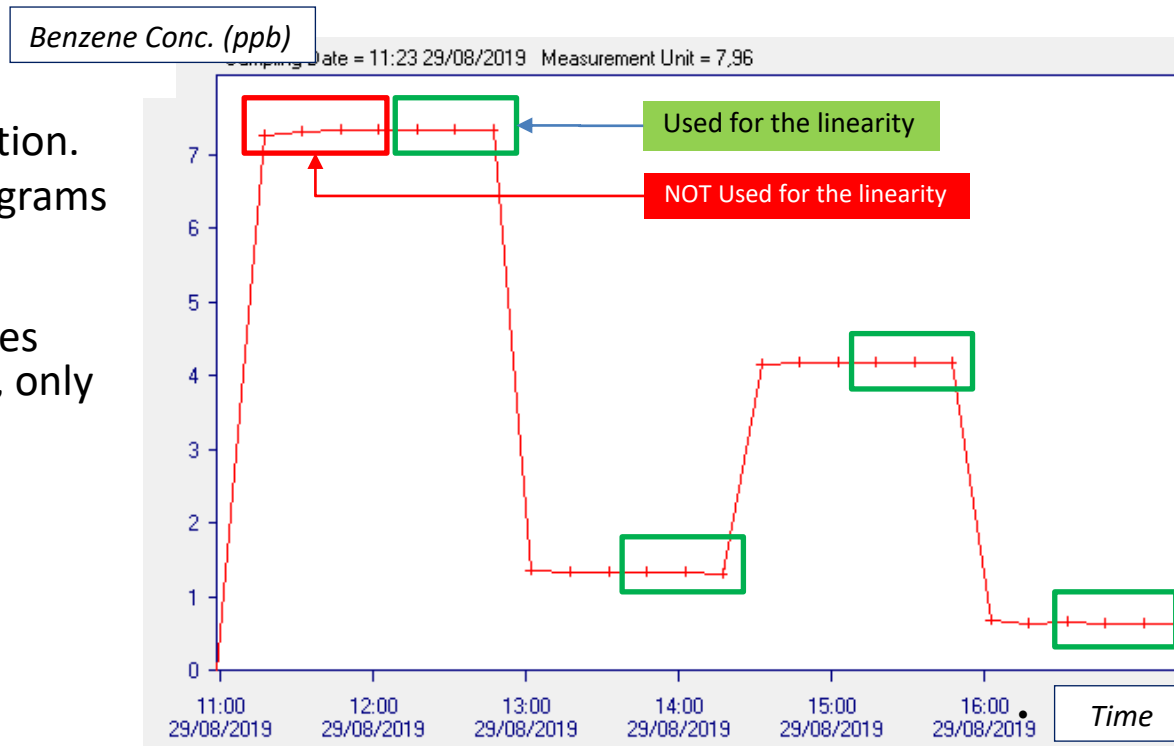
- Number of repetitions for each dilution point:

## *Description of the test, written in the Norm :*

*“For each concentration (including zero), **at least** four individual measurements have to be done. The first measurement of each series must be excluded from the calculation of the regression function.”*

## Advices :

- Do more cycles for each concentration.
- Do not consider the first chromatograms obtained. Consider only the last chromatograms
- Example : in the Mcerts test, 6 cycles (30min for one cycle) were started, only the last 4 cycles were considered

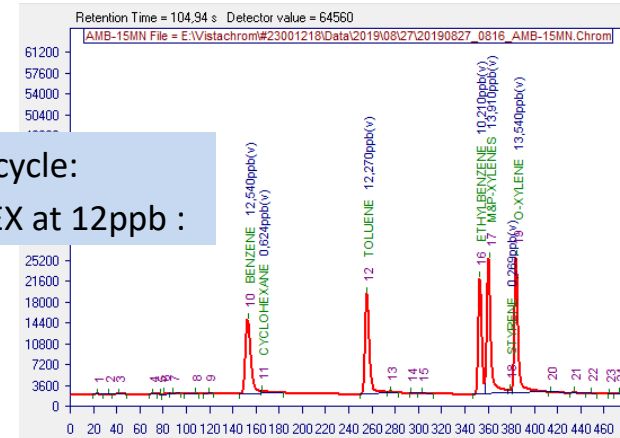


# Precautions to take before starting the test

- **Test of the dilution point : “zero air” used for the linearity (0% of the range)**

*The carry over caused by the diluted system is sometimes not negligible!*

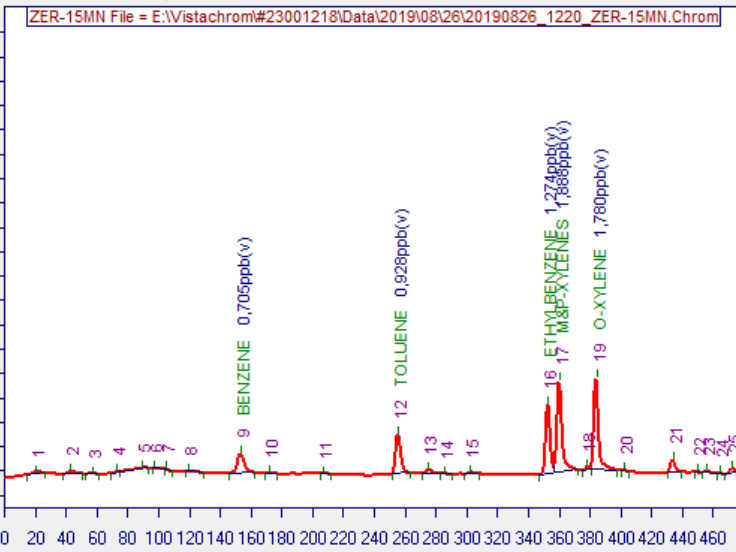
1<sup>st</sup> cycle:  
BTEX at 12ppb :



2nd cycle: zero air (analyzed through the diluting system)

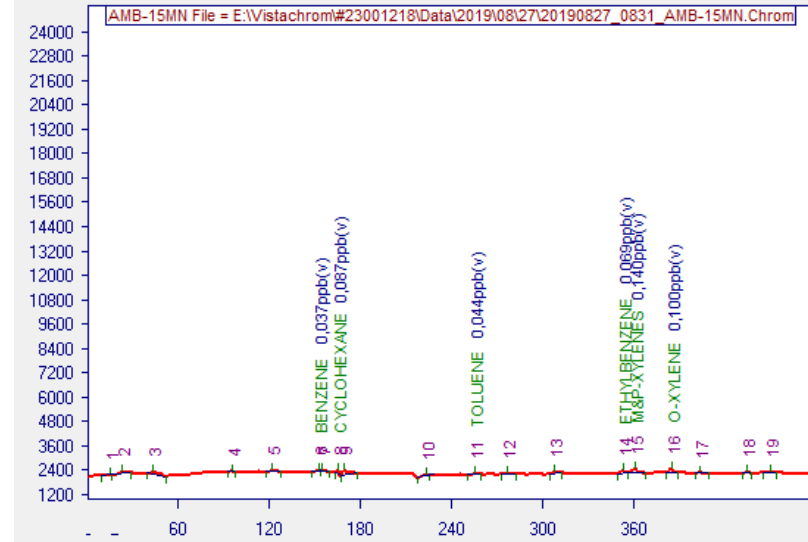
2nd cycle: zero air (analyzed directly, by-passing the diluting system)

Retention Time = 332,31 s Detector value = 19163



➡ Important carry over coming from the dilutor

Retention Time = 269,03 s Detector value = 21220



➡ Negligible carry over, relative to the GC

# Examples of results obtained

- AirToxic #25460719 : on site linearity test

	Awaited Concentration (ppb)	Measured Concentration(ppb)	Predicted Concentration (ppb)	Residual ppb	Abs (Residual ppb)	Residual (relative) %	Reference value (rC, rel)	Reference value (rC, zero)	Test passed
Point 1	0.000	0.010	-0.036	0.045	0.045	X	X	0.154	Yes
Point 2	1.559	1.455	1.531	-0.076	0.076	4.864	5.000	X	Yes
Point 6	5.136	5.041	5.124	-0.083	0.083	1.607	5.000	X	Yes
Point 3	7.726	7.965	7.725	0.240	0.240	3.105	5.000	X	Yes
Point 7	10.329	10.214	10.340	-0.127	0.127	1.229	5.000	X	Yes

Some linearity tests give sometimes good raw results

# Examples of results obtained

- AirToxic #25470719 : on site linearity test

Sometimes, we have to consider the precision of the uncertainty of the diluting system to pass the test successfully:

	Awaited Concentration (ppb)	Measured Concentration(ppb)	Predicted Concentration (ppb)	Residual ppb	Abs (Residual ppb)	Residual (relative) %	Reference value (rC, rel)	Reference value (rC, zero)	Test passed
Point 1	0.003	0.004	-0.152	0.153	0.153	X	X	0.154	Yes
Point 2	1.534	1.345	1.438	-0.067	0.067	4.286	5.000	X	Yes
Point 6	5.186	4.915	5.084	-0.169	0.169	3.293	5.000	X	Yes
Point 3	7.726	7.680	7.725	-0.044	0.044	0.575	5.000	X	Yes
Point 7	10.329	10.507	10.379	0.127	0.127	1.233	5.000	X	Yes

Considering the uncertainty of the two MFC used for the dilution, here are the awaited concentrations “updated”

# Some « tricks » to help you to pass the test

## 1. Optimize the integration of the peaks :

- Apply a new set of “slope” and “drift” parameters to integrate again the peaks
- Or use the option “integrate manually” available in Vistachrom 1.5.

## 2. Use a small “Area Offset”, tuning the substance table:

Substances table information

Substances table name:  Author:

For the analyzer serial number:  Analyzer type:

Substances

#	Name	RT Min	RT Max	Select Peak	GC Result formula	With X=
1	BENZENE	89	99	Middle	X	(Area+200)/BS
2	CYCLOHEXANE	100	110	Middle	$3.8 * X^{0.88}$	Area/BS
3	TOLUENE	370	380	Middle	$1.8 * X^{0.88}$	Area/BS
4	ETHYLBENZENE	580	590	Middle	$2.1 * X^{0.88}$	Area/BS
5	M&P-XYLENES	598	608	Middle	$1.9 * X^{0.81}$	Area/BS
6	STYRENE	625	635	Middle	$2.4 * X^{0.78}$	Area/BS
7	O-XYLENE	635	645	Middle	$2.2 * X^{0.84}$	Area/BS

Curve response of detector

Linear

Factor \* X

With X = (Area + AreaOfs) / BS

Name	Value
Factor	1
AreaOfs	200

## 3. Before starting the linearity test on an AirToxic (using a Photolonisation Detector), check carefully the sensitivity drift : acceptable criterion 10% per day.